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TEMPERATURE AND COMPOSITION OF A PLASMA OBTAINED BY
SEEDING A CYANOGEN-OXYGEN FLAME WITH CESIUM

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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SUMMARY

The temperature and composition of a cyanogen-oxygen flame seeded with cesium are calculated approximately by assuming that the combustion is adiabatic and that the product mixture is in thermodynamic equilibrium. For initial mole fractions of cesium up to 0.1 and flame pressures from 0.01 to 1 atmosphere, electron concentrations up to 4.4×10^{16} per cubic centimeter and plasma temperatures in the range of 4,000° to 5,000° K are obtained.

INTRODUCTION

A plasma with a sufficiently high concentration of electrons for experimental work is of interest in connection with magneto-gas-dynamic research. Probably the best chemical means available for producing a plasma consists of seeding a high-temperature flame with a gas whose ionization potential is low. It was suggested by Robert V. Hess of the Gas Dynamics Branch of Langley Research Center that seeding the combustion products of cyanogen with alkali metals should yield very high electron concentrations. Subsequent unpublished, approximate calculations performed by Hess and Stuart Patterson showed that electron concentrations of the order of 10^{16} per cubic centimeter could be obtained even with potassium as the seeding material.

It is shown in reference 1 that temperatures in the neighborhood of 5,000° K are produced in the combustion of a stoichiometric mixture of cyanogen and oxygen. The flame has nearly the highest temperature known to be obtainable by a chemical reaction. The postcombustion mixture consists chiefly of carbon monoxide CO and nitrogen N₂. Since the physical properties of the CO molecule are generally similar to those of the N₂ molecule, the mixture closely resembles pure nitrogen and, therefore, is to some extent similar to air. A convenient choice of material with low ionization potential is the alkali metal cesium.

The present paper extends the nonseeded, cyanogen-oxygen flame-temperature calculations of reference 1 to cases for which the total pressure is 0.01 to 1 atm and for which the initial mole fraction of cesium is from 0 to 0.1. The partial pressures of the principal species present in the postcombustion mixture are presented along with the electron concentration.

SYMBOLS

| | |
|----------|--|
| e | base of natural logarithms |
| h_I | precombustion enthalpy per unit mass of mixture |
| h_{II} | postcombustion enthalpy per unit mass of mixture |
| H_i | enthalpy per mole of particles of the i th species |
| h | Planck's constant, 6.62517×10^{-27} erg sec |
| I | ionization energy per mole of Cs |
| I' | ionization energy per atom of Cs |
| k | Boltzmann's constant, 1.38044×10^{-16} erg/ $^{\circ}$ K |
| K_i | equilibrium constant (pressure) for dissociation ($i = 1, 2, 3$) or ionization ($i = 5$) of the i th species |
| m_i | mass of molecules of i th species |
| M_i | mass per mole of i th species |
| M_I | mass per mole of precombustion mixture |
| M_{II} | mass per mole of postcombustion mixture |
| n_i | number of moles of i th species per unit mass of mixture |
| N_e | number of electrons per unit volume |
| p_i | partial pressure of i th species |
| p | total pressure |

| | |
|----------------|---|
| p_f | fictitious pressure |
| q_i | partition function for one particle of i th species |
| $q_5^{(elec)}$ | electronic partition function for the cesium atom |
| R | universal gas constant per mole |
| T | absolute temperature |
| T_b | boiling point of cesium at total pressure p |
| U_i | internal energy per mole of i th species |
| $U_5^{(elec)}$ | internal energy per mole of cesium due to electronic excitation |
| V | volume |
| α | initial (precombustion) mole fraction of Cs |
| ϵ_j | excitation energy of the j th electronic state of the cesium atom |
| v_i | number of particles of i th species in volume V |
| ρ | density of postcombustion mixture |
| Subscripts: | |
| λ | C_2N_2 , cyanogen |
| μ | O_2 , diatomic oxygen |
| 1 | CN, cyanogen radical |
| 2 | N_2 , diatomic nitrogen |
| 3 | CO, carbon monoxide |
| 4 | C, atomic carbon |
| 5 | Cs, atomic cesium |

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6 N, atomic nitrogen

7 O, atomic oxygen

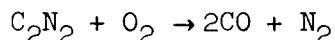
8 e^- , free electron

9 Cs^+ , cesium ion

ASSUMPTIONS

The calculation contained herein is based upon the following assumptions:

Cyanogen C_2N_2 and oxygen O_2 are introduced at room temperature ($298.16^\circ K$) in stoichiometric proportion corresponding to the highly exothermic chemical reaction:



Cesium is introduced in monatomic vapor form at a temperature T_b , the boiling point of liquid cesium corresponding to the flame total pressure. The low dissociation energy (0.49 electron volt) of Cs_2 together with the temperatures (e.g., $T_b = 986^\circ K$ at $p = 1 \text{ atm}$) and the pressures concerned assure the preponderance of the monatomic form in the cesium vapor introduced.

It is also assumed that: (1) the gases are thermally perfect, (2) the enthalpy per unit mass of mixture is the same after combustion as before combustion, (3) the gas mixture reaches thermodynamic equilibrium, and (4) the total pressure is the same after combustion as before combustion.

INITIAL ENTHALPY OF MIXTURE

The components of the precombustion mixture are listed in table I.

TABLE I

| Molecule | Mole fraction introduced | Temperature |
|----------|---------------------------|--------------------------|
| C_2N_2 | $\frac{1}{2}(1 - \alpha)$ | 298.16° K |
| O_2 | $\frac{1}{2}(1 - \alpha)$ | 298.16° K |
| Cs | α | T_b |

Hence, the mass per mole of precombustion mixture is

$$M_I = \frac{1}{2}(1 - \alpha)M_\lambda + \frac{1}{2}(1 - \alpha)M_\mu + \alpha M_5 \quad (1)$$

The number of moles of cyanogen C_2N_2 introduced per unit mass of mixture is then

$$n_\lambda = \frac{\frac{1}{2}(1 - \alpha)}{M_I}$$

Consequently, the enthalpy (per unit mass of mixture) of cyanogen introduced is

$$n_\lambda H_\lambda = \frac{\frac{1}{2}(1 - \alpha)H_\lambda}{M_I}$$

where H_λ is the enthalpy per mole of C_2N_2 at 298.16° K . The enthalpies (per unit mass of mixture) of oxygen O_2 and cesium Cs can be derived in a similar way.

Therefore, the total enthalpy per unit mass of precombustion mixture is

$$h_I = \frac{1}{M_I} \left[\frac{1}{2}(1 - \alpha)H_\lambda + \frac{1}{2}(1 - \alpha)H_\mu + \alpha H_5 \right] \quad (2)$$

where H_λ and H_μ correspond to 298.16° K and H_5 corresponds to the temperature T_b .

It is convenient to refer the enthalpy of cesium to the ideal gas enthalpies of the Cs^+ ions and the free electrons at 0°K . Then, the enthalpy per mole of Cs at temperature T_b is adequately approximated by setting

$$H_5 = \frac{5}{2} RT_b - I \quad (3)$$

where I is the ionization energy per mole of Cs. (The corresponding enthalpies, per mole, of Cs^+ and e^- are then $\frac{5}{2} RT$ each, where T is the temperature of the postcombustion mixture.) The molar enthalpies of C_2N_2 and O_2 must be consistent in reference levels with the enthalpies of the postcombustion species CN , N_2 , CO , C , N , and O . (The minor species NO , CO_2 , O^- , etc. were found to be negligible in the present calculation.)

FINAL ENTHALPY OF MIXTURE

The enthalpy per unit mass of the postcombustion mixture is given by

$$h_{\text{II}} = \sum_{i=1}^9 n_i H_i = \frac{p}{\rho} + \sum_{i=1}^9 n_i U_i \quad (4)$$

where each H_i corresponds to the final temperature T of the mixture.

The mass per mole of postcombustion mixture is

$$M_{\text{II}} = \sum_{i=1}^9 \frac{p_i}{p} M_i \quad (5)$$

Moreover, the number of moles of the i th species per unit mass of mixture is

$$n_i = \frac{1}{M_{\text{II}}} \frac{p_i}{p} \quad (6)$$

Therefore, equations (4) and (6) yield

$$h_{II} = \frac{1}{M_{II}} \sum_{i=1}^9 \frac{p_i}{p} H_i \quad (7)$$

In accordance with the discussion centering around equation (3), the molar enthalpy H_5 of atomic cesium in the final mixture is

$$H_5 = \frac{5}{2} RT + U_5^{(elec)} - I \quad (8)$$

where $U_5^{(elec)}$, the internal energy per mole of cesium due to electronic excitation, is given by (cf. appendix)

$$U_5^{(elec)} = RT^2 \frac{\partial}{\partial T} \log q_5^{(elec)}$$

$$= \frac{R}{k} \left(\frac{\epsilon_1 e^{-\frac{\epsilon_1}{kT}} + 2\epsilon_2 e^{-\frac{\epsilon_2}{kT}} + 2\epsilon_3 e^{-\frac{\epsilon_3}{kT}} + 3\epsilon_4 e^{-\frac{\epsilon_4}{kT}}}{1 + e^{-\frac{\epsilon_1}{kT}} + 2e^{-\frac{\epsilon_2}{kT}} + 2e^{-\frac{\epsilon_3}{kT}} + 3e^{-\frac{\epsilon_4}{kT}}} \right)$$

The molar enthalpies of e^- and Cs^+ are given by

$$H_8 = H_9 = \frac{5}{2} RT \quad (9)$$

while the molar enthalpies H_1 , H_2 , H_3 , H_4 , H_6 , and H_7 of CN, N_2 , CO, C, N, and O, respectively, are given in reference 2.

In accordance with the assumption of adiabatic combustion at constant pressure, the mixture enthalpy per unit mass is the same before and after combustion; that is,

$$h_I = h_{II} \quad (10)$$

where h_I and h_{II} are given by equations (2) and (7).

THERMODYNAMIC EQUILIBRIUM RELATIONS

The relative numbers of atoms present in the mixture follow from table I and are listed in table II.

TABLE II

| Atom | Relative number introduced |
|------|------------------------------|
| C | $(1 - \alpha)/(3 - 2\alpha)$ |
| N | $(1 - \alpha)/(3 - 2\alpha)$ |
| O | $(1 - \alpha)/(3 - 2\alpha)$ |
| Cs | $\alpha/(3 - 2\alpha)$ |

In following a standard procedure of physical chemistry, a fictitious "atomic" pressure p_f is introduced, and table II is used to write the following equations relating the partial pressures p_i of the principal species present in the postcombustion mixture. (These equations account for the conservation of all atoms of carbon, nitrogen, oxygen, and cesium, respectively.)

$$\left. \begin{aligned} p_1 + p_3 + p_4 &= \frac{1 - \alpha}{3 - 2\alpha} p_f \\ p_1 + 2p_2 + p_6 &= \frac{1 - \alpha}{3 - 2\alpha} p_f \\ p_3 + p_7 &= \frac{1 - \alpha}{3 - 2\alpha} p_f \\ p_5 + p_8 &= \frac{\alpha}{3 - 2\alpha} p_f \end{aligned} \right\} \quad (11)$$

In the last equation, which represents the conservation of cesium, the partial pressure of Cs^+ , namely p_9 , has been replaced by its equal, the partial pressure of e^- , that is, p_8 . Thus, the total pressure equation can be written

$$p_1 + p_2 + p_3 + p_4 + p_5 + p_6 + p_7 + 2p_8 = p \quad (12)$$

The reactions to be considered (and their respective equilibrium constants K_i , $i = 1, 2, 3, 5$) are:

$\text{CN} \rightleftharpoons \text{C} + \text{N}$ (dissociation of CN),

$$K_1 = \frac{p_4 p_6}{p_1} \quad (13)$$

$\text{N}_2 \rightleftharpoons 2\text{N}$ (dissociation of N_2),

$$K_2 = \frac{p_6^2}{p_2} \quad (14)$$

$\text{CO} \rightleftharpoons \text{C} + \text{O}$ (dissociation of CO),

$$K_3 = \frac{p_4 p_7}{p_3} \quad (15)$$

$\text{Cs} \rightleftharpoons \text{Cs}^+ + e^-$ (ionization of Cs),

$$K_5 = \frac{p_8 p_9}{p_5} = \frac{p_8^2}{p_5} \quad (16)$$

By using these expressions for the K_i , the partial pressures of the diatomic molecules and the cesium atoms can be eliminated from the four equations (11). Thus,

$$\left. \begin{aligned} \frac{p_4 p_6}{K_1} + \frac{p_4 p_7}{K_3} + p_4 &= \frac{1 - \alpha}{3 - 2\alpha} p_f \\ \frac{p_4 p_6}{K_1} + 2 \frac{p_6^2}{K_2} + p_6 &= \frac{1 - \alpha}{3 - 2\alpha} p_f \\ \frac{p_4 p_7}{K_3} + p_7 &= \frac{1 - \alpha}{3 - 2\alpha} p_f \\ \frac{p_8^2}{K_5} + p_8 &= \frac{\alpha}{3 - 2\alpha} p_f \end{aligned} \right\} \quad (17)$$

Values for the equilibrium constants K_1 , K_2 , and K_3 are given in reference 2. Note, however, that the definition of K_2 in equation (14) differs from the equilibrium constant defined for the reaction $N_2 \rightleftharpoons 2N$ in reference 2. The equilibrium constant K_5 is given by

$$K_5 = \frac{2}{q_5^{(elec)}} \left(\frac{2\pi}{h^2} \frac{m_8 m_9}{m_5} \right)^{3/2} (kT)^{5/2} e^{-\frac{I'}{kT}} \quad (18)$$

Equation (18) is derived in the appendix.

SOLUTION OF THE SIMULTANEOUS EQUATIONS

Equations (10), and (12) to (17) constitute ten equations in the ten unknowns p_1 , p_2 , . . . p_8 , p_f , and T . The total pressure p and the initial cesium mole fraction α enter as parameters. (The fictitious pressure p_f , which could have been eliminated immediately, affords the convenience of a Lagrangian undetermined multiplier.)

A practicable procedure for solving the simultaneous equations is the following:

(1) Select the total pressure p and the initial cesium mole fraction α .

(2) Estimate the partial pressures p_i ($i = 4, 6, 7$), fictitious pressure p_f , and temperature T .

(3) Solve the first three of equations (17) for p_4 , p_6 , and p_7 by an extension of Newton's method of successive approximation. (In the event that the convergence is slow because the iterative character is oscillatory, it may be advantageous to use corrections less than the full Newtonian ones.)

(4) Compute the corresponding values of the remaining partial pressures from the fourth of equations (17) and equations (13) to (16).

(5) Equation (12) generally will not be satisfied. Repeat steps 3 and 4 with a new value of p_f until equation (12) is satisfied.

(6) Equation (10) generally will not be satisfied. Repeat steps 3, 4, and 5 with a new value of T until equation (10) is satisfied.

The computing time is much shortened by making careful estimates of the trial values. Extrapolations become possible as the computation proceeds.

RESULTS OF THE CALCULATION

The calculation has been carried through for four values of the total pressure and six values of the initial mole fraction of cesium, namely, $p = 1, 0.2, 0.05, 0.01$ atm and $\alpha = 0, 0.02, 0.04, 0.06, 0.08, \text{ and } 0.1$. The results are presented in table III and figures 1 to 3. In addition to the postcombustion temperature and partial pressures of the principal species the electron concentration

$$N_e = \frac{p_8}{kT}$$

has been included in the table in cgs units (electrons cm^{-3}). (To convert p_8 from atm to dynes/ cm^2 , multiply by 1.01325×10^6 .)

Figure 1 shows that the addition of cesium to the extent of 0.1 mole fraction results in a lowering of the flame temperature by approximately 300°K at each of the four pressures considered. The greatest electron concentrations in the cases considered occur when $p = 1$ atm, but somewhat greater efficiency of ionization of the cesium is obtained at the lower pressures. To a first approximation, the principal species present in the postcombustion mixture (aside from Cs, Cs^+ , and e^-) are CO and N_2 , followed in decreasing prevalence by N, O, and so forth. As the total pressure is lowered from 1 atm to 0.01 atm the temperature drops by approximately 500°K for any fixed value of α in the range considered.

The maximum electron concentration obtainable at $p = 1$ atm must occur for α greater than 0.1 and probably is of the order of 5×10^{16} electrons cm^{-3} (cf. fig. 2), but the computations have not been extended to verify this.

Figure 3 shows that for small values of α and for low pressures, the electron mole fraction is independent of the pressure. In such cases, the ionization is practically complete. (See table III.)

Langley Research Center,
National Aeronautics and Space Administration,
Langley Field, Va., February 10, 1960.

APPENDIX

DERIVATION OF EXPRESSION FOR K_5 FROM SAHA'S EQUATION

In a given volume V , let

ν_5 = number of Cs atoms

ν_8 = number of free electrons

ν_9 = number of Cs^+ ions

I' = ionization energy per Cs atom

Then (cf. ref. 3),

$$\frac{\nu_8 \nu_9}{\nu_5} = \frac{q_8 q_9}{q_5} e^{-\frac{I'}{kT}}$$

where

$$q_8 = 2 \frac{(2\pi m_8 kT)^{3/2}}{h^3} V$$

$$q_9 = \frac{(2\pi m_9 kT)^{3/2}}{h^3} V$$

$$q_5 = q_5^{(\text{elec})} \frac{(2\pi m_5 kT)^{3/2}}{h^3} V$$

$$q_5^{(\text{elec})} = 2 + 2e^{-\frac{\epsilon_1}{kT}} + 4e^{-\frac{\epsilon_2}{kT}} + 4e^{-\frac{\epsilon_3}{kT}} + 6e^{-\frac{\epsilon_4}{kT}}$$

But,

$$p_i V = \nu_i kT \quad (i = 5, 8, 9)$$

Hence,

$$\frac{v_8 v_9}{v_5} = \frac{p_8 p_9}{p_5} \frac{v}{kT} = K_5 \frac{v}{kT}$$

and

$$K_5 = \frac{(q_8/v) (q_9/v)}{q_5/v} kTe^{-\frac{I'}{kT}}$$

$$= \frac{2}{q_5} \frac{2\pi}{h^2} \frac{m_8 m_9}{m_5} (kT)^{5/2} e^{-\frac{I'}{kT}}$$

which is the desired equation (18).

The preceding derivation accounts for the excited electronic states of the cesium atom but neglects those of the cesium ion since the latter are practically inaccessible in the temperature range of interest here.

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TABLE III.- TEMPERATURE AND COMPOSITION OF CYANOGEN-OXYGEN FLAME SEEDED WITH CESIUM

| P, atm | α | T, °K | CN | N ₂ | CO | C | Cs | N | O | e ⁻ | Cs ⁺ | Ne, cm ⁻³ |
|--------|---|------------------------|--------|----------------|--------|--------|--------|--------|--------|----------------|------------------------|------------------------|
| | | | | | | | | | | | | |
| 1.00 | { 0.00 .02 .04 .06 .08 .10 | 4.85 × 10 ³ | 0.002 | 0.322 | 0.652 | 0.005 | 0.003 | 0.013 | 0.006 | 0.010 | 0.010 | 1.6 × 10 ¹⁶ |
| | | | .001 | .317 | .640 | .004 | .010 | .017 | .017 | 2.6 | | |
| | | | .001 | .311 | .628 | .003 | .010 | .008 | .004 | 3.4 | | |
| | | | .001 | .307 | .618 | .002 | .018 | .007 | .003 | 3.9 | | |
| | | | .001 | .301 | .607 | .002 | .029 | .006 | .003 | 4.4 | | |
| .20 | { .00 .02 .04 .06 .08 .10 | 4.70 | .0003 | .0632 | .1290 | .0014 | .0040 | .0017 | .0024 | .0024 | 3.8 × 10 ¹⁵ | |
| | | | .0003 | .0628 | .1277 | .0011 | .0002 | .0032 | .0014 | 6.9 | | |
| | | | .0002 | .0613 | .1244 | .0008 | .0010 | .0025 | .0011 | 9.5 | | |
| | | | .0002 | .0596 | .1222 | .0006 | .0021 | .0020 | .0008 | 11.5 | | |
| | | | .0002 | .0587 | .1202 | .0005 | .0036 | .0016 | .0006 | 13.4 | | |
| .05 | { .00 .02 .04 .06 .08 .10 | 4.56 | .0001 | .0584 | .1177 | .0004 | .0054 | .0013 | .0005 | .0079 | .0079 | 1.0 |
| | | | .0001 | .0156 | .0321 | .0005 | .0000 | .0013 | .0004 | 2.0 | | |
| | | | .0001 | .0151 | .0314 | .0004 | .0001 | .0011 | .0003 | 2.8 | | |
| | | | .0000 | .0149 | .0308 | .0003 | .0003 | .0007 | .0002 | 3.6 | | |
| | | | .0000 | .0147 | .0297 | .0002 | .0005 | .0005 | .0002 | 4.2 | | |
| .01 | { .00 .02 .04 .06 .08 .10 | 4.38 | .0000 | .0145 | .0292 | .0001 | .0008 | .0004 | .0001 | .0024 | .0024 | 2.1 × 10 ¹⁴ |
| | | | .00001 | .00306 | .00634 | .00012 | .0000 | .00034 | .00012 | 4.3 | | |
| | | | .00001 | .00301 | .00622 | .00009 | .0000 | .00028 | .00010 | 6.5 | | |
| | | | .00001 | .00297 | .00611 | .00007 | .00001 | .00023 | .00008 | 8.5 | | |
| | | | .00001 | .00294 | .00600 | .00006 | .00002 | .00017 | .00006 | 10.3 | | |

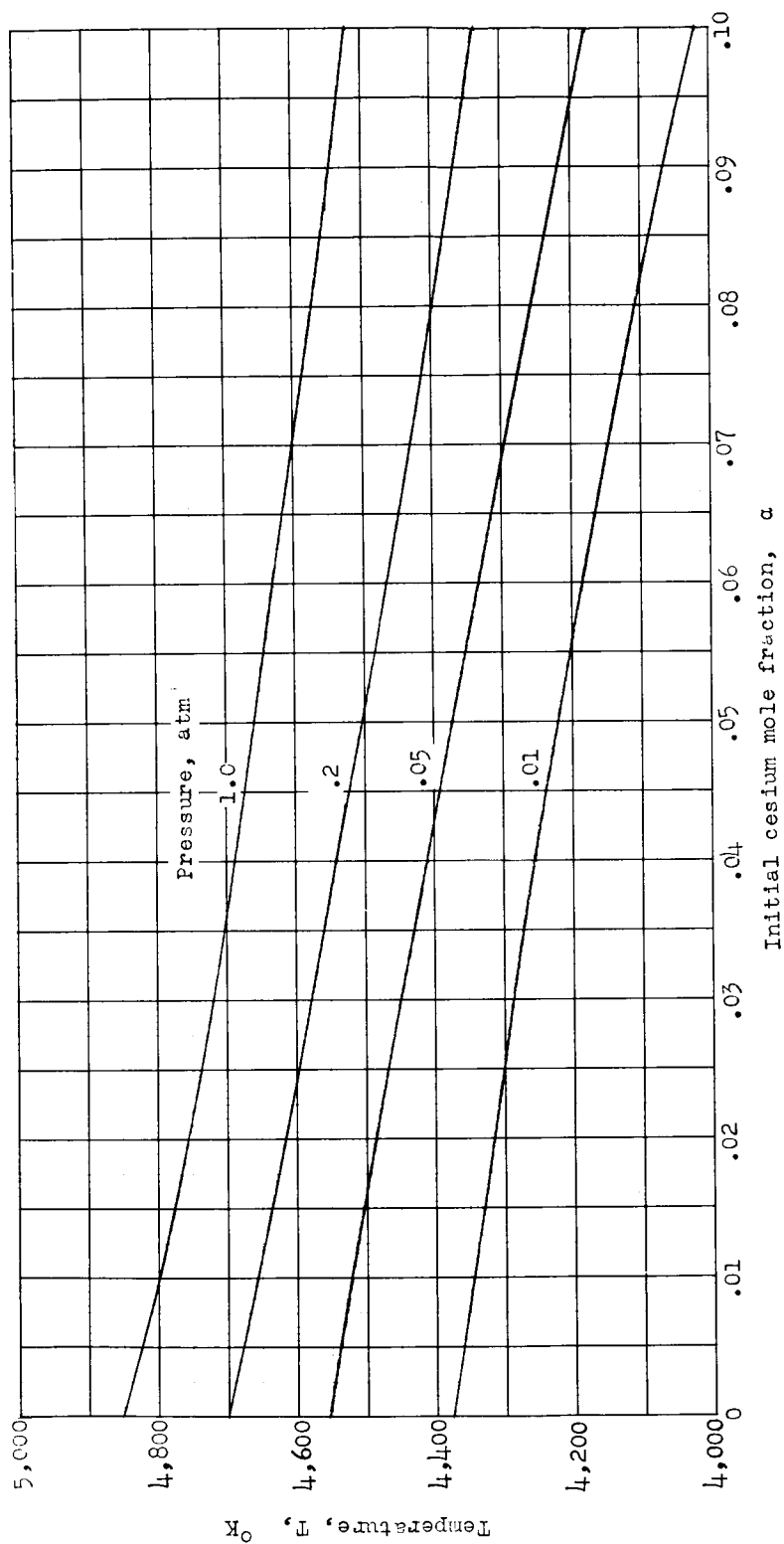


Figure 1.- Variation of temperature with initial cesium mole fraction for various values of total pressure.

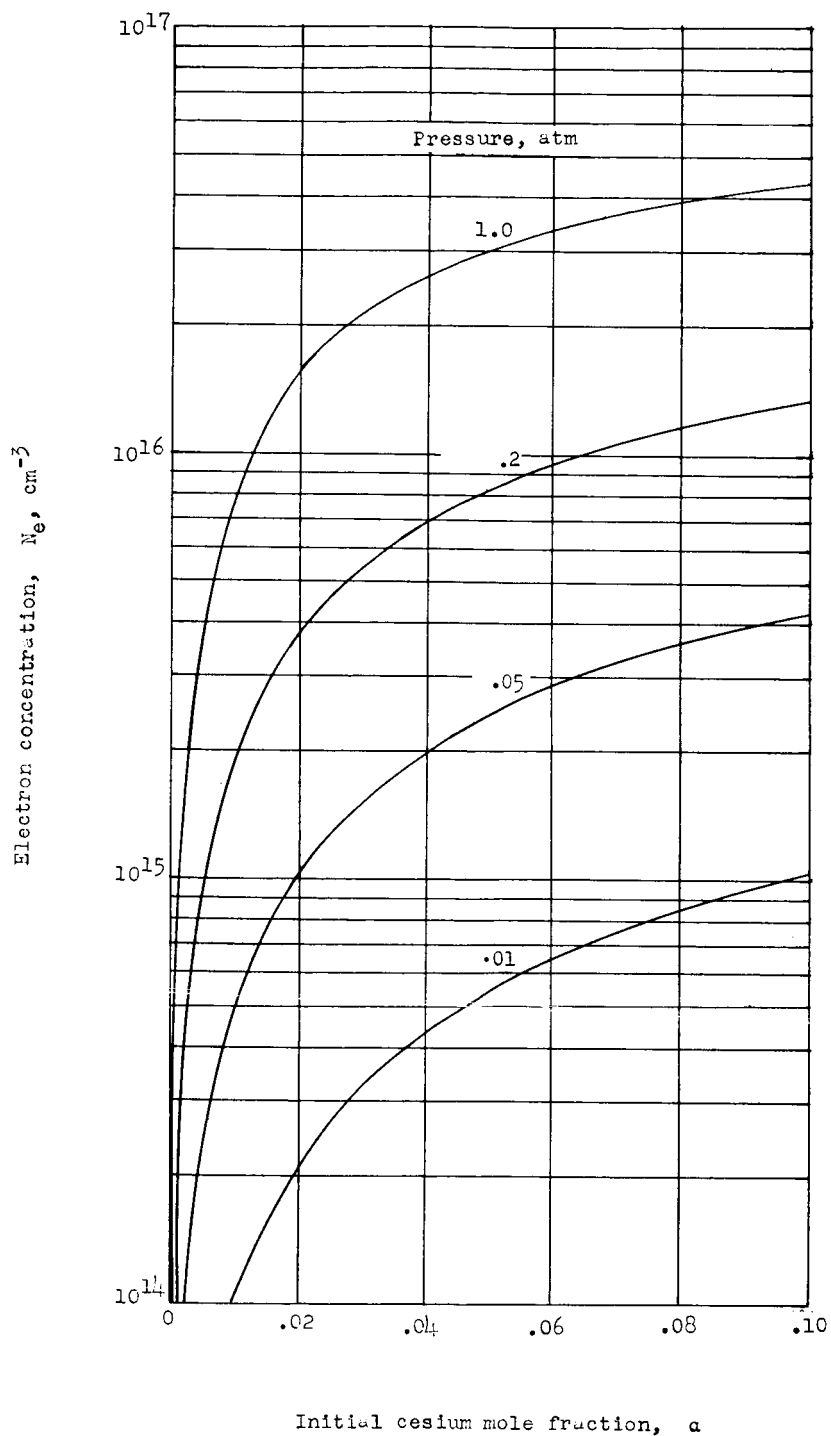


Figure 2.- Variation of electron concentration with initial cesium mole fraction for various values of total pressure.

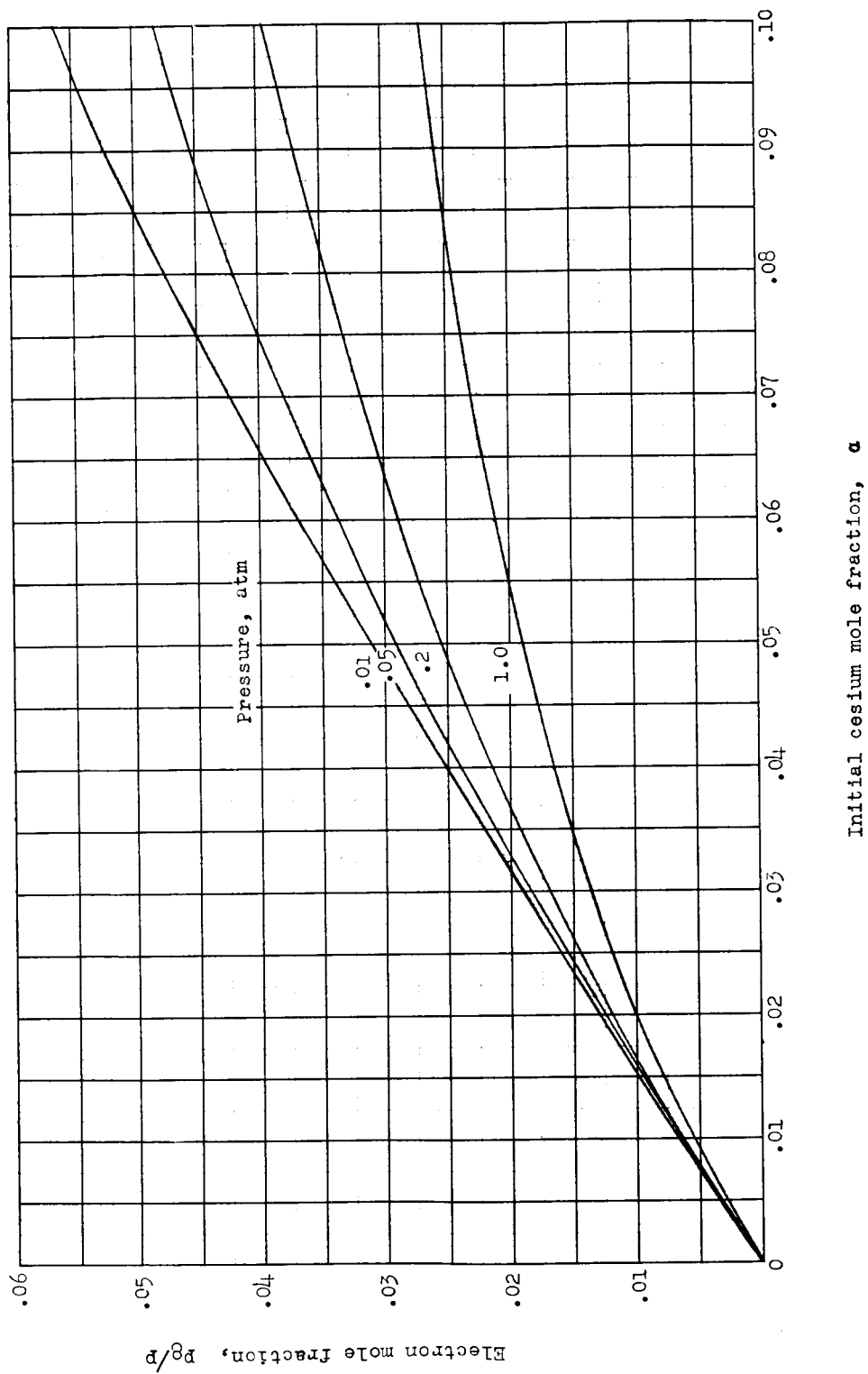


Figure 3.- Variation of electron mole fraction with initial cesium mole fraction for various values of total pressure.